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PART II

ENVIRONMENTAL PROTECTION AGENCY

■

ANALYSIS OF POLLUTANTS

Proposed Test Procedures

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 130]

ANALYSIS OF POLLUTANTS

Proposed Test Procedures

Notice is hereby given that the regulations set forth in tentative form below are proposed by the Environmental Protection Agency. The proposed regulations set forth, pursuant to section 304(g) of the Federal Water Pollution Control Act Amendments of 1972 (86 Stat. 816 et seq. Public Law 92–500 (1972) hereinafter referred to as the "Act"), required test procedures for the analysis of pollutants.

Section 304(g) of the Act states that "The Administrator shall, within one hundred and eighty days from the date of enactment of this title, promulgate guidelines establishing test procedures for the analysis of pollutants that shall include factors which must be provided in any certification pursuant to section 401 of this Act or permit application pursuant to section 402 of this Act." These proposed guidelines require that the measurements listed below be performed by the test procedures indicated. As the result of extensive laboratory comparisons, both inhouse and with extramural public and private participants, it is believed that these procedures generally yield the most accurate results. However, it is recognized that other methods have been and are being used to perform these measurements. It is also recognized that under certain circumstances it may be advantageous to use methods other than those indicated. Accordingly, the use of other methods is permitted if approved by the Regional Administrator of the region in which such use will occur. It is anticipated that procedures will be promulgated for a number of additional measurements in the near future. Even then, however, in some cases, applicants for a permit or for certification may be required to submit analyses of pollutants for which measurement techniques are not specified by these or other regulations. In such cases, the Regional Administrator should be consulted as to an appropriate measurement technique for the pollutant and waste discharge involved. Generally, the Regional Administrator will require evidence of acceptability as described herein but may waive this requirement if the proposed method is known to him to be acceptable when applied to a *specific* waste effluent. However, should there be a subsequent contest as to the actual composition and content of any waste effluent, the indicated procedures or their automated versions will be the reference methods for the settlement of all actions related thereto.

On April 19, the Administrator promulgated regulations specifying forms and procedures for the submission of applications for permits under § 402 of the FWPCA. These regulations included required techniques for a number of measurements required to be performed in connection with permit applications. Where the attached regulations specify a measurement technique, the April 19 regulations are superseded. Where, however, a measurement technique is set forth in the April 19 regulations, and no technique for the same measurement is included in these regulations, the April 19 procedures will continue to apply.

Prior to the adoption of the proposed regulations, consideration will be given to any comments, suggestions, or objections thereto which are submitted in writing to the Office of Research and Development, Office of Monitoring Systems, Division of Equipment and Techniques, Washington, D.C. 20460 by (45 days from the publication date).

Dated: June 22, 1973.

ROBERT W. FRI,
Acting Administrator,
Environmental Protection Agency.

PART 130—TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

Sec.
130.1 Applicability.
130.2 Definitions.
130.3 Identification of procedures.
130.4 Application for alternative test procedures.
130.5 Requirement of alternative test procedures.
130.6 Requirement of additional test procedures.
Appendix I—Determination of median and range of values.
Appendix II—Previously unpublished test procedure.

AUTHORITY: Section 304(g) of the Federal Water Pollution Control Act Amendments of 1972 (86 Stat. 816 *et seq.*, Public Law 92–500).

§ 130.1 Applicability.

The procedures prescribed herein shall be used to perform the measurements indicated whenever the waste constituent specified is required to be measured for:

(a) An application for a permit under section 402 of the Federal Water Pollution Control Act, as amended,

(b) Reports required to be submitted by dischargers under the National Pollutant Discharge Elimination System (NPDES) established by Parts 124 and 125 of this chapter, and

(c) Certifications issued by States pursuant to section 401 of the Federal Water Pollution Control Act, as amended.

§ 130.2 Definitions.

(a) "Reference A" means *Standard Methods for the Examination of Water and Wastewater*, 13th Edition, 1971. This publication is available from the American Public Health Association, 1015 18th St., NW., Washington, D.C. 20036.

(b) "Reference B" means *Annual Book of Standards, Part 23, Water; Atmospheric Analysis*, 1972. This publication is available from the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

(c) "Reference C" means *Methods for Chemical Analysis of Water and Wastes*, Environmental Protection Agency, Analytical Quality Control Laboratory, Cincinnati, Ohio. This publication is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 (Stock #5501–0067).

(d) "Reference D" means *"Cold Vapor" Method for Determining Mercury*, 1972; J. F. Kopp, M. C. Longbottom, and L. B. Lobring, Journal American Water Works Association, Vol. 64, No. 1.

§ 130.3 Identification of Procedures.

The measurements shown in below shall be performed by the appropriate reference procedure:

Measurement	*Reference*
Alkalinity	C, p. 6
Ammonia Nitrogen	C, p. 134
Arsenic	A, p. 65, 4a (Digestion); A, p. 62, Method 104A (Measurement)
Boron	A, p. 69
Cadmium	C, p. 83
Chloride	B, p. 21, Method A
Chromium	C, p. 83
Conductance, specific	B, p. 163, Method B
Copper	C, p. 83
Fluoride	A, p. 171, Method 121A with p. 174, Method 121C
Hardness	A, p. 179, Method 122A
Iron	C, p. 83
Magnesium	C, p. 83
Manganese	C, p. 83
Mercury	D
Nitrate Nitrogen	A, p. 458, Method 213B
Nitrogen, total kjeldahl	A, p. 469, Method 216
Organic Carbon, total	C, p. 221
Organochlorine Pesticides	Appendix II
Orthophosphate	C, p. 243
Oxygen Demand, biochemical	A, p. 489, Method 219
Oxygen Demand, chemical	A, p. 495, Method 220
Phosphorous, total	C, p. 242
Selenium	A, p. 296, Method 150A
Silver	C, p. 83
Solids, total	A, p. 535, Method 224A
Surfactants	A, p. 559, Method 229
Suspended Non-filterable Solids, total	A, p. 537, Method 224C
Temperature	A, p. 559, Method 162
Zinc	C, p. 83

§ 130.4 Application for Alternative Test Procedures.

(a) Any person may apply to the Regional Administrator for authorization to use an alternative test procedure. The Regional Administrator may authorize the use of such alternative procedure where he determines, on the basis of any information available to him, that the procedures would meet the requirements of paragraph (b)(1) and (2) of this section.

(b) Upon receipt of any application, the Regional Administrator shall first determine whether the alternative procedure may be authorized on the basis of information available to him, without further data. If he is unable to authorize the procedure on the basis of such information, he shall notify the applicant that his application can be considered further only after submission of data resulting from the following procedure.

Eleven replicate analyses shall be performed on each of three effluent samples collected during a 24-hour period of continuous discharge and characteristic of the discharge for which the alternative procedure is requested. One sample shall contain the maximum amount of pollutant observed during the 24-hour period. Another sample shall contain the minimum amount observed during such period. The third shall contain an amount approximately intermediate between the maximum and minimum values. The Regional Administrator may authorize the use of an alternative procedure where he determines:

(1) That the median (Appendix I) of each set of eleven values obtained by use of the proposed alternative procedure is within ±10% of the median of the eleven values obtained on the sample, using the required method; and

(2) That the range of values (Appendix I) obtained by the alternative procedure does not exceed 1.2 times the range yielded by the required method for the same sample.

(c) If the discharger wishes to propose an alternate test procedure that he believes to have better absolute accuracy in the measurement of his waste discharge than the reference procedure, he may present to the Regional Administrator test results comparing the reference method to the alternative procedure, based on measurements of solutions of known strength and of "spiked" representative waste samples. The Regional Administrator may, then, on the basis of the presented evidence or any additional evidence he requires, decide to approve or disapprove the proposed alternative test procedure.

(d) If the conditions under which the authorization was granted change in any way which may affect the validity of measurements taken by an approved alternative test procedure, the Regional Administrator may require the discharger to submit further test results or other data. On the basis of such data, or other information available to him, the Regional Administrator may withdraw his approval of any alternative test procedure.

(e) The approval of an alternative test procedure for a particular discharge shall not constitute approval of that procedure for any other discharge. However, information submitted by any applicant or discharger may be considered by the Regional Administrator in determining whether to authorize the use of an alternative test procedure.

§ 130.5 Requirement of alternative test procedures.

Where the Regional Administrator determines, for a particular discharge, that the method required by these regulations would not yield acceptably accurate results, he may require the applicant for certification or for an NPDES permit, to use another method specified by him.

§ 130.6 Requirement of additional test procedures.

Where the Regional Administrator determines, for a particular discharge, that information about a pollutant not included in these regulations is required to properly assess the environmental impact of the discharge, he may require the applicant for certification or for an NPDES permit, to furnish such additional information as specified by him.

APPENDIX I

DETERMINATION OF MEDIAN AND RANGE OF VALUES

The following procedures shall be followed in determining the median and range of values of each set of eleven measurements:

1. List the eleven measurements in ascending order of magnitude.

2. The median is identified as the sixth measurement in the ordered listing.

3. The range of values is the difference between the tenth and second measurements in the ordered listing.

Example (1)—Measurements in the order they are actually obtained from experiments: 10.1, 10.2, 10.2, 10.1, 10.1, 10.2, 10.2, 10.2, 10.1, 10.2, 10.1. In ascending order of magnitude, the order would be as follows:

Order: 1 2 3 4 5 6 7 8 9 10 11

Values: 10.1, 10.1, 10.1, 10.1, 10.1, 10.2, 10.2, 10.2, 10.2, 10.2, 10.2.

Median: The median is the sixth value in the listing, or 10.2.

Range: The range is 0.1, the difference between the tenth value (10.2) and the second value (10.1).

Example (2)—Measurements in the order they are actually obtained from experiments: 5.62, 5.51, 5.58, 5.57, 5.61, 5.52, 5.57, 5.54, 5.60, 5.60, 5.56.

In ascending order of magnitude, the order would be as follows:

Order: 1 2 3 4 5 6 7 8 9 10 11

Values: 5.51, 5.52, 5.54, 5.56, 5.57, 5.57, 5.58, 5.60, 5.60, 5.61, 5.62.

Median: The median is the sixth value in the listing, or 5.57.

Range: The range is 0.09, the difference between the tenth value (5.61) and the second value (5.52).

APPENDIX II

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDUSTRIAL EFFLUENTS

1. *Scope and Application.* 1.1 This method covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in industrial effluents. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorous, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of 1 μg/liter: BHC, lindane, heptachlor, aldrin, heptachlor, epoxide, dieldrin, endrin, Captan, DDE, DDD, DDT, methoxychlor, endosulfan, dichloran, mirex, pentachloronitrobenzene and trifluralin. Under favorable circumstances, Strobane, toxaphene, chlordane (technical grade) and others may also be determined. The usefulness of the method for other specific pesticides must be demonstrated by the analyst before any attempt is made to apply it to sample analysis.

1.3 When organochlorine pesticides exist as complex mixtures, the individual compounds may be difficult to distinguish. High, low, or otherwise unreliable results may be obtained through misidentification and/or one compound obscuring another of lesser concentration. Provisions incorporated in this method are intended to minimize the occurrence of such interferences.

2. *Summary.* 2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through the use of column chromatography and liquid-liquid partition, methods for elimination of nonpesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. *Interferences.* 3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required (1).

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organochlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCB's): Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (2, 3).

3.4 Phthalate Esters: These compounds, widely used as plasticizers respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing. The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorous Pesticides: A number of organophosphorous pesticides, such as those containing a nitro group, e.g., parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the flame photometric detector (4).

4. *Apparatus and Materials.* 4.1 Gas Chromatograph—Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture—Radioactive (tritium or nickel 63).

4.2.2 Microcoulometric titration.

4.2.3 Electrolytic conductivity.

4.3 Recorder—Potentiometric strip chart (10 inch) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing—Pyrex (180 cm long by 4 mm ID).

4.4.2 Glass Wool—Silanized.

4.4.3 Solid Support—Gas-Chrom Q (100–120 mesh).

4.4.4 Liquid Phases—Expressed as weight percent coated on solid support.

4.4.4.1 OV–1, 3%.

4.4.4.2 OV–210, 5%.

4.4.4.3 OV–17, 1.5% plus QF–1, 1.95%.

4.4.4.4 QF–1, 6% plus SE–30, 4%.

4.5 Kuderna-Danish (K–D) Glassware (Kontes).

4.5.1 Snyder Column—three ball (macro) and two ball (micro).

4.5.2 Evaporative Flasks—500 ml.

4.5.3. Receiver Ampuls—10 ml, graduated.

4.5.4 Ampul Stoppers.

4.6 Chromatographic Column—Chromaflex (400 mm long by 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb (special order from Kontes K–420540–9011).

4.7 Chromatographic Column—Pyrex (approximately 400 mm long by 20 mm ID) with coarse fritted plate on the bottom.

4.8 Micro Syringes—10, 25, 50 and 100 μl.

4.9 Separatory Funnels—125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Blender—High speed, glass or stainless steel cup.

4.11 Graduated cylinders—100 and 250 ml.

4.12 Florisil—PR Grade (60–100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil lined screw caps. Before use, activate each in foil-covered glass container overnight in a bath at 130°C. Determine lauric-acid value as in section 13.

5. *Reagents, Solvents, and Standards.* 5.1 Ferrous Sulfate—(ACS) 30% solution in distilled water.

5.2 Potassium Iodide—(ACS) 10% solution in distilled water.

5.3 Sodium Chloride—(ACS) Saturated solution (pre-rinse NaCl with hexane) in distilled water.

5.4 Sodium Hydroxide—(ACS) 10 N in distilled water.

5.5 Sodium Sulfate—(ACS) Granular, anhydrous.

5.6 Sulfuric Acid—(ACS) Mix equal volumes of concentrated H_2SO_4 with distilled water.

5.7 Diethyl Ether—Nanograde, redistilled in glass, if necessary.

5.7.1 Must contain 2% alcohol and be free of peroxides by the following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand for one minute. No yellow color should be observed in either layer.

5.7.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. *CAUTION:* Reaction may be vigorous if the solvent contains a high concentration of peroxides.

5.7.3 Distill deperoxidized ether in glass and add 2% methanol.

5.8 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30–60°C)—nanograde, redistill in glass if necessary.

5.9 Pesticide Standards—Reference grade.

6. *Calibration.* 6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when $\leq$ 0.06 ng is injected for electron capture detection and $\leq$ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements the detector noise level should be less than 2% of full scale and be operated within its linear response range.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard pesticides are shown in Figures 1, 2, 3 and 4 and provide reference operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table 1 as a guide.

7. *Quality Control.* 7.1 Duplicate and spiked sample analyses are recommended as quality control checks. When the routine occurrence of a pesticide is being observed, the use of quality control charts are recommended (5).

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. *Sample Preparation.* 8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5–7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 For a sensitivity requirement of 1 μg/l, when using microcoulometric or electrolytic conductivity methods for detection take 100 ml of sample for analysis. If interferences pose no problem, the sensitivity of the electron capture detector should permit as little as 50 ml of sample to be used. Background information on the extent and nature of interferences will assist the analyst in choosing the required sample size and preferred detector.

8.3 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

9. *Extraction.* 9.1 Add 60 ml of 15% methylene chloride in hexane (v/v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pass the organic layer through a column containing 3 to 4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60 ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract in the K–D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated, see Section 10.

10. *Clean-up and Separation Procedures.* 10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as, the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or effect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition—This procedure is used to remove fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides. Of the pesticides listed in Section 1.2 only mirex is not efficiently recovered.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 40 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30 to 45 seconds. Extract with two 100 ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3 to 4 inch anhydrous sodium sulfate column into a 500 ml K–D flask equipped with a 10 ml ampul. Rinse the separatory funnel and column with three 10 ml portions of hexane.

10.2.4 Concentrate the extracts to 6 to 10 ml in the K–D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil column adsorption chromatography.

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, as described in Section 13) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50 to 60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500 ml K–D flasks equipped with 10 ml ampuls (see Section 10.4). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml. of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether in petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6–10 ml in the K–D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition—By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate. Aldrin, BHC, Chlordane, DDD, DDE, DDT, Heptachlor, Heptachlor Epoxide, Lindane, Methoxychlor, Mirex Pentachloronitrobenzene, Strobane, Toxaphene, Trifluralin, and PCB's.

15% Eluate. Endosulfan I, Endrin, Dieldrin, Dichloran, Phthalate esters.

50% Eluate. Endosulfan II, Captan.

Certain thiophosphate pesticides will occur in each of the above fractions, as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (6).

11. *Calculation of Results.* 11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure as described in reference 1.

11.2 $$\text{Micrograms/liter} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

Where A = ng standard/Standard area, B = Sample aliquot area, V_i = Volume of extract injected (μl), V_t = Volume of total extract (μl), and V_s = Volume of water extracted (ml).

12. *Reporting Results.* 12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Standardization of Florisil Column by Weight Adjustment Based on Absorption of*

Lauric Acid. 13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6, 7). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus: 13.2.1 Buret, 25 ml volume with 1/10 ml graduations.

13.2.2 Erlenmeyer flasks, 125 ml volume with narrow mouth and 25 ml volume, glass stoppered.

13.2.3 Pipet, 10 and 20 ml transfer.

13.2.4 Volumetric flasks, 500 ml volume.

13.3 Reagents and Solvents.

13.3.1 Alcohol, ethyl, USP or absolute, neutralized to phenolphthalein.

13.3.2 Hexane, distilled from all glass apparatus.

13.3.3 Lauric acid, purified, CP.

13.3.4 Lauric acid solution. Transfer 10.000 grams lauric acid to a 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1ml = 20 mg).

13.3.5 Phenolphthalein indicator. Dissolve 1 gram in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. Dissolve 20 grams NaOH (pellets, reagent grade) in water and dilute to 500 ml (1 N). Dilute 25 ml 1 N NaOH to 500 ml with water (0.05 N). Standardize as follows: Weigh 100 to 200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure: 13.4.1 Transfer 2,000 grams of Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 ml of lauric acid solution (400 mg), stopper, and shake occasionally for 15 minutes. Let adsorbent settle and pipet 10.0 ml of supernatant into a 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil. 13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05 N NaOH to a permanent end point

13.5 Calculation of Lauric Acid Value, and adjustment of column weight.

13.5.1 Calculate the amount of lauric acid adsorbed on the Florisil as follows: Lauric Acid Value = mg lauric acid/grams of Florisil = 200—(ml required for titration of X mg lauric acid/ml of 0.05 N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 grams. Verify proper elution of pesticides by Section 13.6 .

13.6 Test for Proper Elution Pattern and Recovery of Pesticides: Prepare a test mixture containing aldrin, heptachlor epoxide, p, p'-DDE, dieldrin, Parathion and malathion. Dieldrin and Parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate, and the others in the 6% eluate.

References

1. "Method for Organic Pesticides in Water and Wastewater," (1971) Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268.

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7. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and its Use in Standardizing Florisil Columns", *Journal of the Association of Official Analytical Chemists, 51,* 29 (1968).

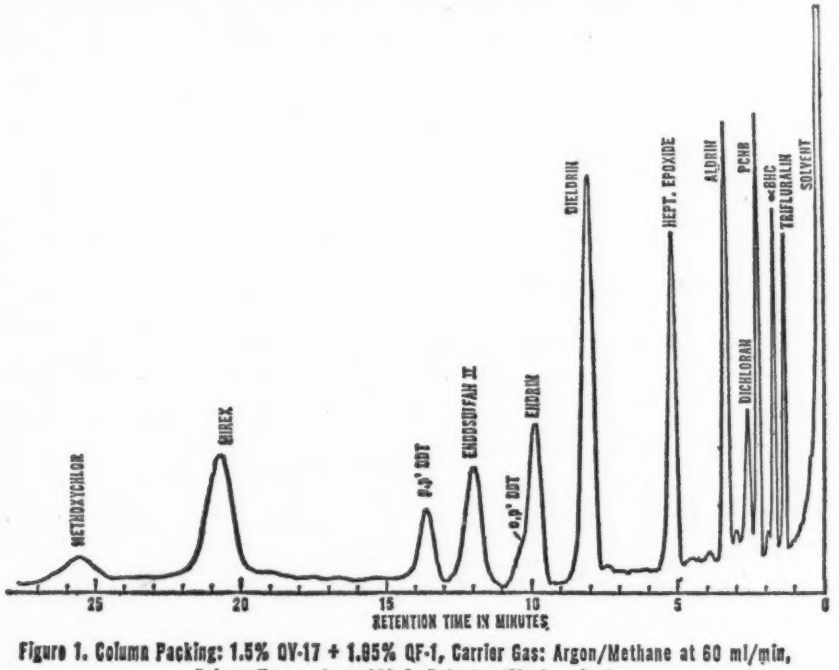

Figure 1. Column Packing: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C., Detector: Electron Capture.

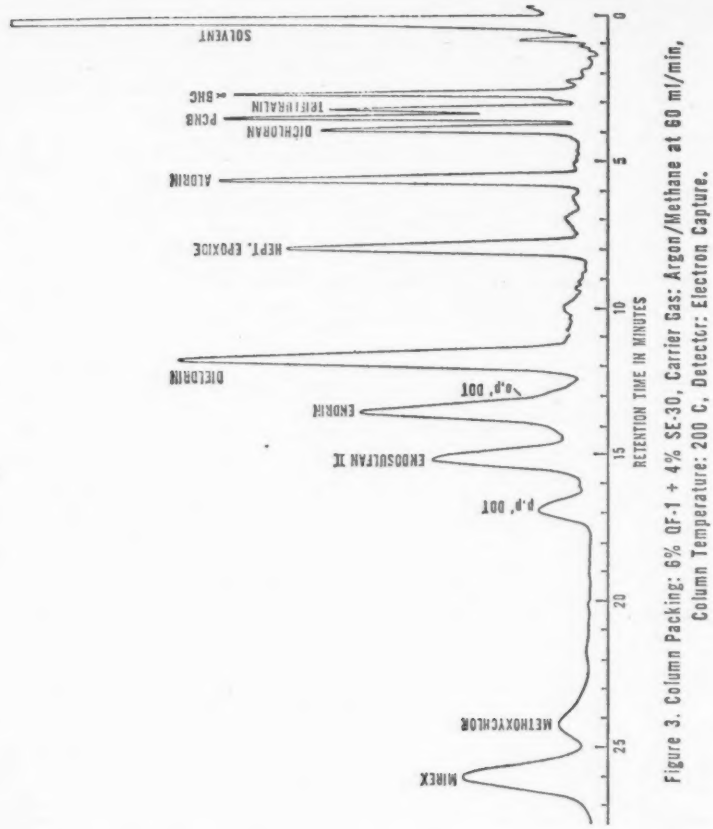

Figure 3. Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

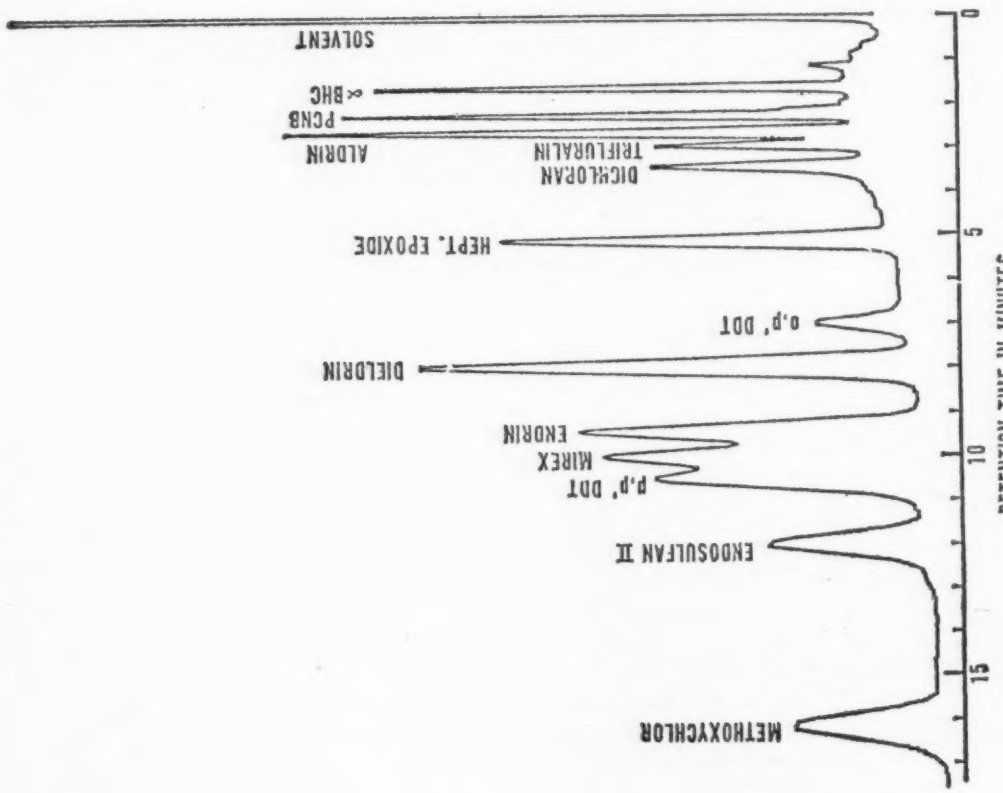

Figure 2. Column Packing: 5% OV-210, Ca rier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

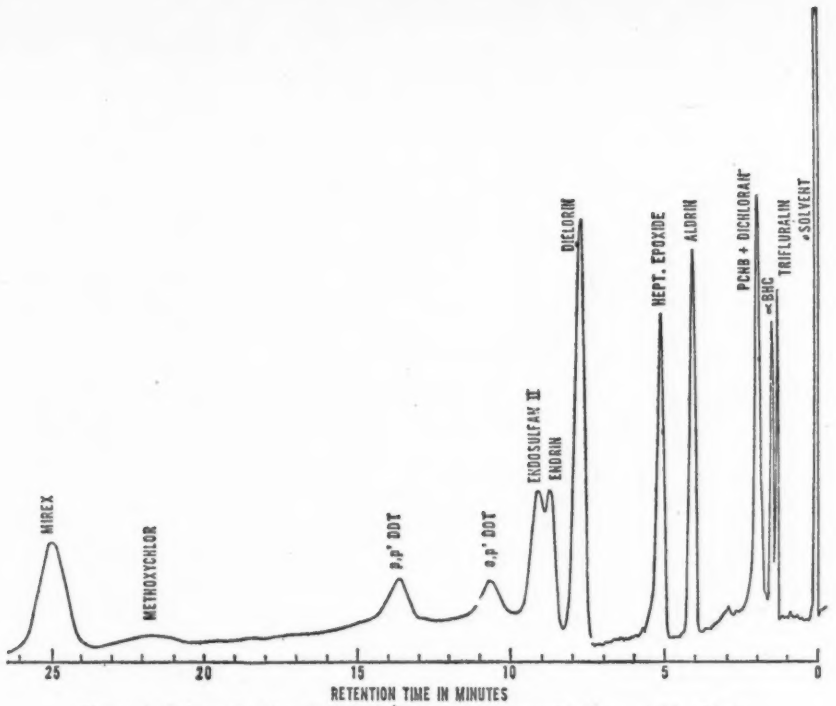

Figure 4. Column Packing: 3% OV-1, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

TABLE 1.—*Retention ratios of various organochlorine pesticides to aldrin*

Liquid Phase [1]	1.5% OV-17 + 2.95% QF-1	5% OV-210	3% OV-1	6% QJ-1 + 4% SE-30
Column Temp	200 C	180 C	180 C	200 C
Argon/Methane Carrier Flow	60 ml/min	70 ml/min	70 ml/min	60 ml/min
Pesticide	RRt	RRt	RRt	RRt
Trifluralin	0.39	1.11	0.33	0.57
α-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor Epoxide	1.54	1.93	1.28	1.43
Thiodan I	1.95	2.48	1.62	1.79
p,p'-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p'-DDT	3.16	2.70	2.69	2.39
p,p'-DDD	3.48	3.75	2.61	2.55
Thiodan II	3.59	4.59	2.25	2.72
p,p'-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min. absolute)	3.5	2.6	4.0	5.6

[1] All columns glass, 180 cm x 4 mm ID, solid support Gas-Chrom Q (100/120 mesh).

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